⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 201 319**
A2

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: 86303450.0

㉒ Date of filing: 07.05.86

⑤① Int. Cl.⁴: C 04 B 35/18

㉚ Priority: 10.05.85 JP 98075/85

㊸ Date of publication of application: 12.11.86 Bulletin 86/46

㊹ Designated Contracting States: BE DE FR GB SE

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⑤④ **Method of producing cordierite ceramics and alpha-alumina for use in the method.**

⑤⑦ A method of producing cordierite ceramics by molding and firing a batch material containing α -alumina, which comprises adjusting the particle size distribution of α-alumina so that the amount of particles having a particle size of not more than 3 µm is not more than 17 wt% and a particle size of 50% by cumulative weight is 4-15 µm. In this way consistent production of ceramics of low thermal expansion and high thermal shock resistance is achieved.

METHOD OF PRODUCING CORDIERITE CERAMICS AND α -ALUMINA FOR USE IN THE METHOD

This invention relates to a method of producing cordierite ceramics having excellent thermal shock resistance, and more particularly to ceramic materials for use in an extrusion molding process.

Since cordierite ceramics have small thermal expansion coefficient, excellent high temperature properties and good surface properties, they are widely used in industry, and particularly honeycomb structural bodies made of cordierite ceramics are used as a catalyst carrier for the purification of automobile exhaust gas, a catalyst carrier for deodorization, a filter for the purification of exhaust gas, a heat exchange structure and so on.

In the production of cordierite ceramics used for such applications, talc, kaolin, silica, alumina, aluminium hydroxide and the like are generally used as a starting material for the formation of cordierite ($2MgO.2Al_2O_3.5SiO_2$). Among these, magnesia material such as talc or the like is disclosed in US Patent No. 4,280,845, and kaolin material is disclosed in US Patent No. 3,885,977. Furthermore, aluminium hydroxide

is generally used as an alumina material. In the latter case, cracks tend to be produced by shrinkage and endothermic reactions in the firing associated with dehydration of aluminium hydroxide. Therefore, a mixture of α -alumina and aluminium hydroxide or α-alumina alone is used as the alumina material.

As a method of producing a honeycomb structural body from the above materials, US Patent No. 3,885,977 discloses the production of the honeycomb body having a low thermal expansion coefficient by an extrusion molding process.

Although thermal shock resistance of about 700-800°C is obtained in such a honeycomb structural body having an outer diameter of 11.8 cm (4.66 inches) and a length of 10 cm (4 inches) as a result of achieving a low thermal expansion in the above conventional technique, there is scattering in the properties of the product when many are produced. Therefore, it is not yet known how consistently to produce cordierite ceramics having a higher thermal shock resistance.

It is an object of the invention to overcome the aforementioned problems and to provide a method of producing cordierite ceramics which have a low thermal expansion coefficient equal to that of the conventional product, a higher thermal shock resistance and a small scattering in properties.

According to the invention, there is provided a method of producing cordierite ceramics by preparing a batch material containing α-alumina for the formation of cordierite, molding and firing it, characterized in that said α-alumina is adjusted to have a particle size distribution of α-alumina that particles having a particle size of not more than 3 μm is not more than 17% by weight and a particle size of 50% by cumulative weight is between 4 μm and 15 μm.

The invention also provides α-alumina as defined herein, for use in the method of the invention.

The invention will now be explained and embodiments described with reference to the accompanying drawings, wherein:-

Figs. 1a and 1b are SEM photographs (secondary electron image) showing granular structures of plate extrusion body and powder of α-alumina material according to the invention, respectively;

Figs. 2a and 2b are SEM photographs (secondary electron image) showing granular structures of plate extrusion body and powder of α-alumina material in the reference example, respectively;

Fig. 3 is a graph showing particle size distributions of α-alumina in the invention and the reference example; and

Fig. 4 is a graph showing a relation between oil absorption and porosity of cordierite ceramic body according to the invention.

The invention involves defining the alumina material for cordierite formation as described above in the method of stably producing cordierite ceramics having a low thermal expansion coefficient and an excellent thermal shock resistance. The reason for the limitations in the invention will be described below.

First, the alumina material is α-alumina because when all the alumina material is aluminium hydroxide, there are problems due to the dehydration reaction during the firing. As α-alumina, it is preferable to use complete α-alumina in which alumina intermediate such as γ-alumina or the like is not identified as a crystal phase. Furthermore, the alumina intermediates produced between aluminium hydroxide and α-alumina such as χ, κ, γ, δ, η, θ-aluminas have high reactivity and adversely affect the cordierite reaction stage as mentioned later, so that they must not be incorporated into the α-alumina.

As to the particle size of α-alumina, when fine particles of not more than 3 μm in size are present, the reaction with talc as a magnesia material proceeds at a relatively low temperature of not more than about 1,300°C and the main reaction between talc and kaolin

for the cordierite formation having a low thermal expansion coefficient is obstructed, so that the amount of fine particles of not more than 3 μm is critical. Particularly, micro-fine particles of not more than 1 μm in size have high reactivity, so that the reaction with the other material such as talc, kaolin or the like proceeds to obstruct the above main reaction, the orientation of the cordierite crystal is degraded, and scattering of thermal shock resistance arises. Consequently, the use of micro-fine particles is not favourable. Further, when the amount of fine particles of not more than 3 μm exceeds 17% by weight, the thermal shock resistance is degraded.

The reason why the particle size of 50% by cumulative weight is between 4 μm and 15 μm is that when this particle size is less than 4 μm, these particles are almost fine and it is very difficult to produce the starting material and the thermal shock resistance is degraded. On the other hand, when this particle size exceeds 15 μm, the reaction temperature for the cordierite formation becomes higher and the thermal expansion coefficient is high and as a result, the thermal shock resistance is degraded. The more preferred size distribution is such that the micro-fine particles of not more than 3 μm in size are not more than 12% by weight and the particle size of 50% by cumulative

weight is between 4 μm and 12 μm. For instance, it is desirable to exclude coarse particles in accordance with the size of slit in the extrusion molding of honeycomb structural bodies.

Preferably, the α-alumina is in the secondary particle form because this suppresses the reaction with talc, kaolin or the like at low temperature and increases the porosity which is useful for a catalyst carrier or a filter. Further the average particle size of the primary particles is preferably limited to 1-5 μm in order to achieve good reactivity in the cordierite formation. When the primary particle size is less than 1 μm, the cordierite formation and the main reaction with talc and kaolin are unfavourably obstructed, while when it exceeds 5 μm, the thermal shock resistance is unfavourably degraded. Moreover, the confirmation of the secondary particles is represented by SEM photograph (secondary electron image) as well as bulk density under pressure (g/cm^3) and oil absorption (ml/100 g) measured under pressurized conditions not breaking secondary particles as physical values showing the form of secondary particle. In the latter case, it is preferable that under a pressure of 1 t/cm^2, the bulk density is not more than 2.25 g/cm^3, and the oil absorption is not less than 18.5 ml/100 g.

The α-alumina is preferably of the sandy type, for the following reason. α-alumina is generally produced by a Bayer process. On the other hand, in order to obtain large α-alumina primary particles, there is usually used so-called flowery type wherein α -alumina is mixed with a fluorine containing mineralizer and fired in a rotary type firing furnace at a relatively low temperature and the resulting aggregate is pulverized. However, since the flowery type α-alumina has a flat crystal structure, a greater amount of micro-fine particles or crystal fragments is liable to be present owing to the pulverizing operation or the like. Such a flowery type α-alumina adversely affects the reaction of cordierite formation. On the other hand, α-alumina obtained by the Bayer process of firing at a relatively high temperature without the mineralizer, i.e. sandy type, has particles wherein the crystal is developed in a direction of C-crystal axis, so that the crystal fragments are hardly produced in the pulverizing and the reactivity with talc or the like at low temperature is small. Therefore, the sandy type is particularly suitable as a starting material for the cordierite formation.

As to the amount of Na_2O in the alumina material, the Bayer process for the manufacture of the alumina includes a step of dissolution of NaOH,

so that the resulting alumina contains Na_2O up to about 0.6 wt% as a total Na_2O(T-Na_2O) of water-soluble Na_2O(W-Na_2O) and insoluble Na_2O. Since the Na_2O component obstructs the reaction of cordierite formation at high temperature, in order to stably obtain a high thermal shock resistance, it is more preferable to use middle or low soda grade of T-Na_2O controlled to less than 0.3%. Moreover, since the contribution of particle size and the like of α-alumina to cordierite reaction is very large, good properties can be obtained even in alumina having an ordinary soda grade of T-Na_2O = about 0.4% through Bayer process.

Example

There was prepared α-alumina materials for Sample Nos. A-S shown in the following Table 1. In this Table, the measurement of particle size was performed by means of a laser particle size analyzer made by C.I.L.A.S. using sodium hexametaphosphate as a dispersion agent. Further, the measurement of oil absorption was carried out according to JIS K5421 and K5101. In addition, the primary particle size was measured by SEM photograph. Moreover, among the above samples, the granular structures in plate extrusion body and powder of α-alumina itself as Sample No. C, which is within the range of the invention, are shown in

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Figs. 1a and 1b as SEM photograph, while the granular structures of plate extrusion body and powder as Sample No. P, which is outside the range of the invention, are shown in Figs. 2a and 2b as SEM photograph. Furthermore, curves of particle size distribution in Sample Nos. C and P are shown in Fig. 3.

Table 1

No.	Fluorine mineralizer S (sandy type) F (flowery type)	Amount of T-Na_2O (wt%)	Particle size			Oil adsorption (ml/100 g)
			secondary particles		primary particle size on average (μm)	
			3 μm ≧ (wt%)	particle size of 50% by cumulative weight (μm)		
A	S	0.26	10.5	6.3	0.8	21.1
B	"	0.26	11.1	6.4	1.0	20.5
C	"	0.24	10.8	6.7	2.0	21.8
D	"	0.23	10.8	8.5	5.0	21.6
E	"	0.24	10.5	8.8	6.0	21.9
F	"	0.26	12.0	7.1	2.2	20.8
G	"	0.23	15.0	5.7	2.4	19.3
H	"	0.25	17.0	4.0	2.4	19.0
I	"	0.25	18.5	3.7	2.2	18.3
K	"	0.22	10.7	8.0	2.6	21.9
L	"	0.22	10.0	15.0	2.6	20.5
M	"	0.23	8.5	17.0	2.4	24.0
N	F	0.26	10.0	6.5	2.4	22.0
O	"	0.25	16.8	6.5	2.2	19.5
P	"	0.25	21.4	4.5	2.2	18.1
Q	S	0.45	11.5	6.0	2.2	21.5
R	F	0.37	27.0	3.8	2.0	18.0
S	"	0.19	32.7	3.5	2.6	17.8

Each of α-alumina materials shown in Table 1 was mixed with a cordierite base selected from combinations I-III of talc, kaolin and so on as shown in the following Table 2. The resulting cordierite was extrusion-molded into a honeycomb structural body having an outer diameter of 11.8 cm (4.66 inches), a length of 10 cm (4 inches) and a cell density of 6 mil/400 CPI^2, which was fired under firing conditions shown in Table 2. Moreover, the α-alumina was subjected to a sieving treatment at 105 μm before the mixing, but in this case the particle size was the same as in Table 1. In addition, the chemical composition and particle size of the starting materials shown in Table 2 are shown in the following Table 3.

Table 2

	Composition (wt%)							Firing conditions
	talc	calcined talc	kaolin	calcined kaolin	alumina	aluminum hydroxide	silica	
I	40.2	-	25.2	21.1	13.5	-	-	1410°C × 4H
II	19.0	19.0	21.4	20.0	4.5	16.1	-	1395°C × 4H
III	39.2	-	21.8	-	11.5	17.8	10.0	1410°C × 6H

Table 3

(wt%)

	Ig·loss	SiO_2	Al_2O_3	MgO	Fe_2O_3	TiO_2	CaO	Na_2O	K_2O
talc	5.2	61.9	0.7	31.8	0.6	-	0.1	-	-
calcined talc	-	66.1	0.2	33.6	0.1	-	0.1	-	-
kaoline	13.8	45.5	38.9	-	0.3	1.2	0.2	0.1	-
calcined kaolin	-	52.4	44.9	-	0.5	1.8	-	0.1	0.1
aluminum hydroxide	33.7	-	64.8	-	-	-	-	0.4	-
silica	0.1	99.7	-	-	0.1	-	-	-	-
alumina A-S (average value)	-	-	99.3	-	-	-	-	0.3	-

The evaluation results are shown in the following Table 4. In Table 4, the value of thermal expansion coefficient (CTE) from 40°C to 800°C is a value at 50 mm in length in the extrusion direction of the honeycomb, the spalling strength in electric furnace shows a temperature wherein cracks are produced when the sample is held in the electric furnace at a given temperature (step-up from 700°C at a rate of 25°C) for 20 minutes and taken out therefrom at room temperature. Furthermore, ◎ is very good, o is good, and x is bad in the evaluation column. Moreover, Fig. 4 shows a relation between the porosity shown in Table 4 and the oil absorption shown in Table 1.

Table 4

No.	Condition for the formation of base	Alumina used	CTE ($\times 10^{-6}$/°C, 40-800°C)	Spalling strength in electric furnace (n=2-5 average × °C)	Porosity (%)	Evaluation	Remarks
1	I	A	0.72	770	34.7	×	
2	"	B	0.60	850	34.3	◎	
3	"	C	0.50	910	35.0	◎	
4	"	D	0.63	840	34.9	○	
5	"	E	0.80	780	35.0	×	
6	"	F	0.57	860	34.4	◎	
7	"	G	0.68	810	33.1	○	
8	"	H	0.68	800	32.4	○	
9	"	I	0.81	750	31.2	×	
10	"	K	0.62	870	35.0	◎	
11	"	L	0.68	820	34.2	○	
12	"	M	0.75	780	35.5	×	
13	"	N	0.58	840	35.2	○	
14	"	O	0.70	810	33.4	○	
15	"	P	0.84	750	30.9	×	
16	"	Q	0.62	880 (830-900)	34.8	○	large scattering
17	"	R	0.92	730	30.7	×	
18	"	S	0.95	700	30.4	×	
19	II	C	0.63	880	-	◎	
20	"	F	0.63	870	-	◎	
21	"	I	0.83	770	-	×	
22	III	C	0.48	920	-	◎	
23	"	F	0.54	890	-	◎	
24	"	I	0.79	750	-	×	

As is apparent from the above, cordierite ceramics using α-alumina material with particle size defined in the invention are very good or good in the evaluation, while the thermal shock resistance is poor in case of using α-alumina material having a particle size outside the range of the invention.

As mentioned above, according to the method of the invention, cordierite ceramics having a low thermal expansion coefficient equal to that of the conventional product, a high thermal shock resistance and a small scattering in properties can be produced by specifying the particle size distribution of α -alumina as the starting material. Therefore, ceramic honeycomb structural bodies having an excellent thermal shock resistance can stably be produced by using α -alumina having particle size defined in the invention as the starting material.

CLAIMS

1. A method of producing cordierite ceramics by preparing a batch material containing α-alumina for the formation of cordierite, molding and firing it, characterized in that said α-alumina has a particle size distribution of α-alumina such that particles having a particle size of not more than 3 μm are present in an amount of not more than 17% by weight and the particle size of 50% by cumulative weight is between 4 μm and 15 μm.

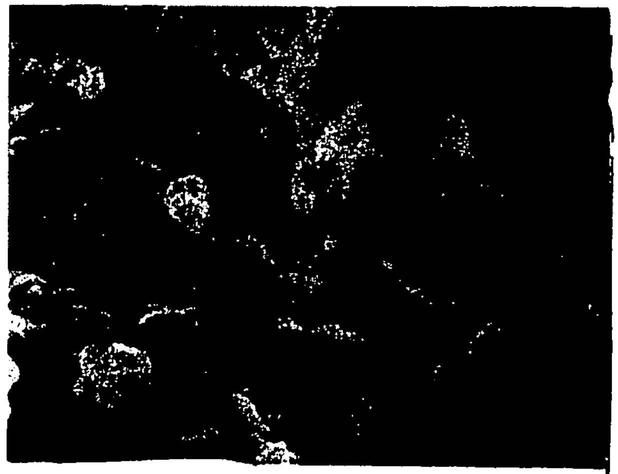
2. A method according to claim 1, wherein said α-alumina is secondary particles having a primary α-alumina average particle size in the range 1 to 5 μm.

3. A method according to claim 1 or claim 2, wherein said α-alumina is sandy type α-alumina.

4. A method according to any one of claims 1 to 3 wherein said cordierite ceramics is a ceramic honeycomb structural body.

5. α-alumina for use in the method of claim 1 having a particle size distribution such that particles having a particle size of not more than 3 μm are present in an amount of not more than 17% by weight and the particle size of 50% by cumulative weight is between 4 μm and 15 μm.

FIG_1a



(x3500)

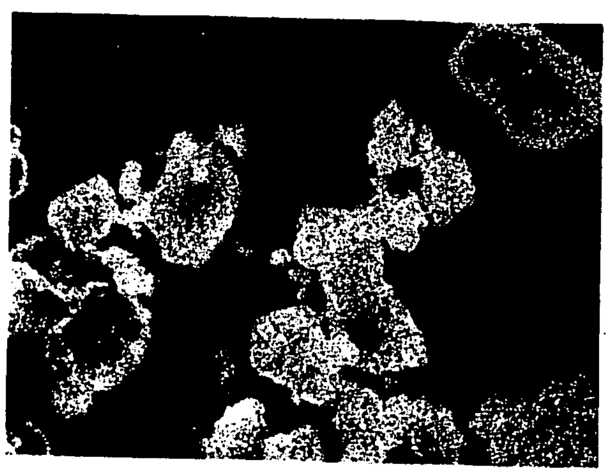
FIG_1b

(x3500)

FIG_2a

(x 3500)

FIG_2b



(x 3500)

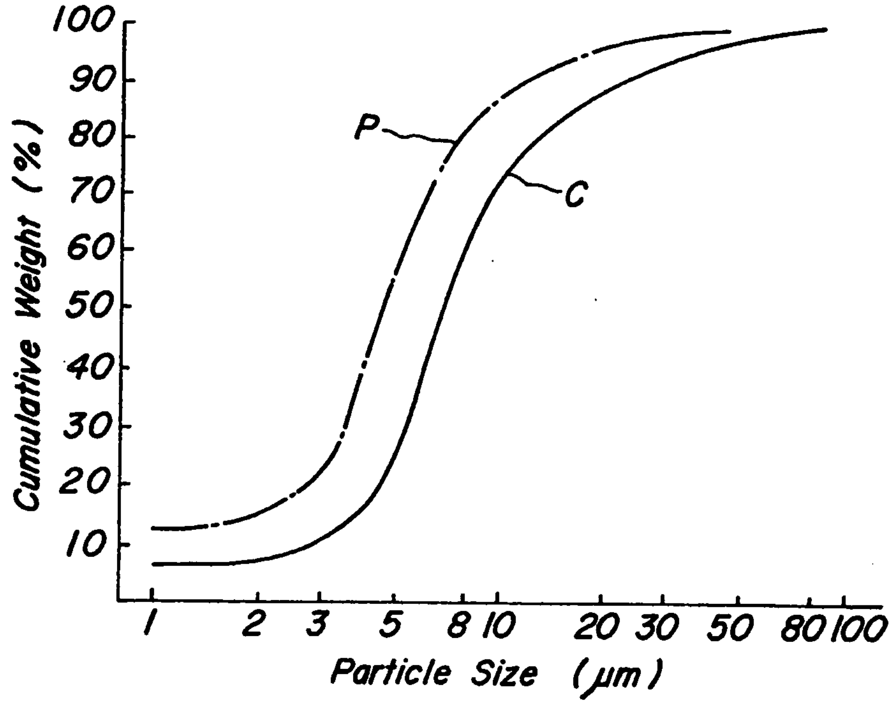

100
90
80
70
60
50
40
30
20
10
Cumulative Weight (%)
P
C
1
2
3
5
8
10
20
30
50
80
100
Particle Size (μm)

FIG. 3

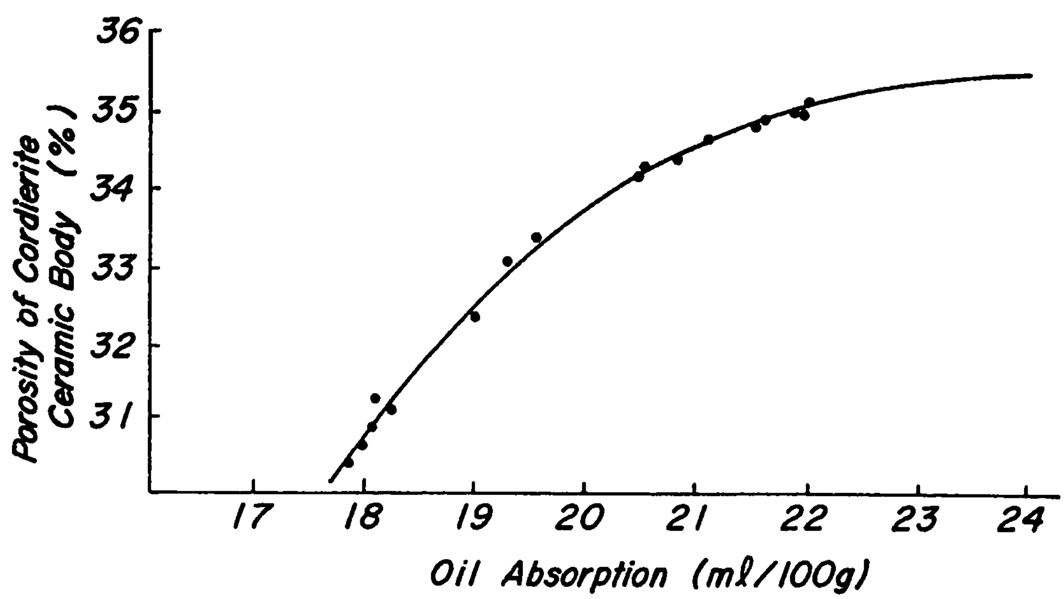

36
35
34
33
32
31
Porosity of Cordierite Ceramic Body (%)
17
18
19
20
21
22
23
24
Oil Absorption (ml/100g)

FIG. 4